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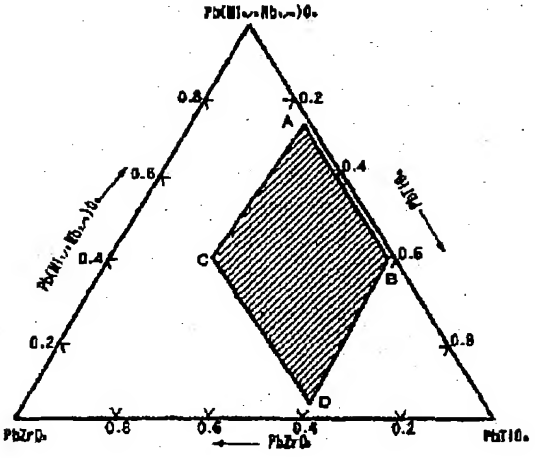
(54)【発明の名称】　圧電磁器組成物

(57)【要約】　(修正有)

【目的】　低温で焼結可能で比抵抗が大きく、かつ、圧電歪定数が大きいアクチュエータ、特に積層型圧電素子用材料の提供する。

【構成】　一般式(1-w){xＰｂ（Ｎｉ$_{1/3}$Ｎｂ$_{2/3}$）Ｏ$_3$－ｙＰｂＴｉＯ$_3$－ｚＰｂＺｒＯ$_3$}－ｗＰｂ（Ｍｅ$_{1/2}$Ｗ$_{1/2}$）Ｏ$_3$(x+y+z=1)で示され、配合比x,y,zが、この３成分組成図において、以下の組成点Ａ：(X=0.74,y=0.25,z=.001)　Ｂ：(x=0.40,y=0.59,z=0.01)　Ｃ：(x=0.40,y=0.25,z=0.35)Ｄ：(x=0.06,y=0.59,z=0.35)を結ぶ線上およびこの線に囲まれる範囲にあり、かつwが、0.001≦w≦0.2の範囲にあり、ＭｅがＮｉ，Ｍｇ，Ｃｕ，Ｚｎ，Ｃｏのいずれか一種であり、かつＭｎ，Ｃｒ，Ｆｅの少なくとも一種をそれぞれＭｎＯ$_2$，Ｃｒ$_2$Ｏ$_3$，Ｆｅ$_2$Ｏ$_3$に換算して、０．００５～１．０重量％含有し、さらに主成分中のＰｂの一部を０．００１～０．２のＣａ，Ｂａ，Ｓｒの内少なくとも一種で置換。



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【特許請求の範囲】

【請求項1】　一般式(1-w){xPb($Ni_{1/3}Nb_{2/3}$)O_3－yPbTiO_3－zPbZrO_3}－wPb($Me_{1/2}W_{1/2}$)O_3(x+y+z=1)で示され、配合比x，y，zが、この3成分組成図において、以下の組成点A：(X=0.74，y=0.25，z=.001) B：(x=0.40，y=0.59，z=0.01)　C：(x=0.40，y=0.25，z=0.35)　D：(x=0.06，y=0.59，z=0.35)を結ぶ線上およびこの線に囲まれる組成範囲にあり、かつwが、0.001≦w≦0.2の範囲にあり、MeがNi，Mg，Cu，Zn，Coのいずれか一種であり、かつMn，Cr，Feの少なくとも一種をそれぞれMnO_2，Cr_2O_3，Fe_2O_3に換算して、0.005～1.0重量%含有することを特徴とする圧電磁器組成物。

【請求項2】　Pbの一部が0.001～0.2のCa，Ba，Srの内の少なくとも一種で置換されていることを特徴とする請求項1記載の圧電磁器組成物。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明はチタン酸ジルコン酸鉛を主成分とする圧電磁器組成物に関するものであり、特に圧電特性が大であると共に、焼結温度が1100℃程度と低く、かつ、絶縁性能に優れた圧電磁器組成物に関するものである。

【0002】

【従来の技術】従来圧電磁器組成物としては、チタン酸ジルコン酸鉛を主成分とするものが圧電定数が大であるために、圧電振動子を初めとしてアクチュエータ用の材料として広く利用されている。しかしながらこの系の材料は、焼成時における酸化鉛の蒸発に起因して緻密な焼結体が得にくいこと、モルフォトピック相境界（MPB）近傍において圧電性がチタニウムとジルコニウム組成に依存するため、特性の再現性と均一性を保証しにくいという欠点がある。このような欠点を改良するため、例えばPbの一部を適量のCa，Sr，Mg，Ba等で置換する手段、若しくはLa，Nd，Nb，Ta，Sb，Bi，Th，W等の酸化物を添加する手段がある。前者によれば圧電特性を低下させずに誘電率を大とすることができ、後者によれば分極が容易となり圧電定数が増大し、経時変化が小さくなるという利点がある。

【0003】一方、上記チタン酸ジルコン酸鉛の改良と平行してABO_3型の強誘電体としてA若しくはBの位置に原子価の異なる複数のイオンを持つ複合ペロブスカイト型化合物が数多く発見された。以後、この複合ペロブスカイト型化合物との三成分の組成に対する研究開発が精力的に進められている。前記三成分系の圧電磁器組成物として、例えばPb($Ni_{1/3}Nb_{2/3}$)O_3－PbTiO_3－PbZrO_3なる組成のものがある。このような三成分系の圧電磁器組成物の特徴は、前記の成分系の例えばPb(Zr，Ti)O_3と比較して、酸化鉛の蒸発が

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少なく、焼成が容易であると共に、モルフォトピック相境界（MPB）が点から線に拡大し、より広い用途に適合する特性を持つ材料が得られることである。

【0004】前記Pb($Ni_{1/3}Nb_{2/3}$)O_3－PbTiO_3－PbZrO_3系の圧電磁器組成物は圧電歪定数（d定数）が極めて大きいことから、アクチュエータ素子用の圧電磁器に適している。

【0005】

【発明が解決しようとする課題】しかしながら、前記Pb($Ni_{1/3}Nb_{2/3}$)O_3－PbTiO_3－PbZrO_3系の圧電磁器組成物の焼結温度は1200～1300℃と高温である。このため、この圧電磁器組成物で積層型圧電素子を作成する場合には、内部電極としてこの焼結温度に耐え得る白金やパラジウムを利用せねばならず、製造コストが高いという問題があった。焼結温度を低くすることができれば、安価な銀・パラジウム合金等が利用可能となる。銀・パラジウム合金を内部電極として用いる場合、パラジウムのコストが高いこと及びパラジウムの含有量が多い場合にはパラジウムが焼結中に酸化還元反応を起こし、積層型圧電素子中に亀裂や剥離を生じさせることから、パラジウムの割合が30%以下であることが要求される。

【0006】パラジウムの比率を30%以下にするには、Ag－Pd系相図より、焼結温度を1150℃以下、望ましくは1120℃以下とすることが必要である。このため、Pb($Ni_{1/3}Nb_{2/3}$)O_3－PbTiO_3－PbZrO_3系の圧電磁器組成物で内部電極に銀・パラジウムを用いた積層型圧電素子を作成するには仮焼粉を微粉砕したり、あるいはHIP処理するといった煩雑な操作を必要とした。さらに、前記Pb($Ni_{1/3}Nb_{2/3}$)O_3－PbTiO_3－PbZrO_3系の圧電磁器組成物は、比抵抗が比較的小さく、このため例えば、積層型圧電素子のように一層の厚みが100μm前後の素子に前記Pb($Ni_{1/3}Nb_{2/3}$)O_3－PbTiO_3－PbZrO_3系の圧電磁器組成物が使用された場合、印加できる電圧が小さく充分な性能が引き出せない、あるいは使用中に絶縁破壊してしまう等、信頼性が低いという問題があった。

【0007】本発明は、上記従来技術に存在する問題点を解決し、圧電特性が大であると共に、焼結温度が1100℃程度と低温であり、かつ、比抵抗が大でアクチュエータ用材料、特に積層型圧電素子用材料に適した圧電磁器組成物を提供することを目的とする。

【0008】

【問題を解決するための手段】上記問題を解決するために、本発明においては、一般式(1-w){xPb($Ni_{1/3}Nb_{2/3}$)O_3－yPbTiO_3－zPbZrO_3}－wPb($Me_{1/2}W_{1/2}$)O_3(x+y+z=1)で示され、配合比x，y，zが、この3成分組成図において、以下の組成点A：(X=0.74，y=0.25，z=.001)　B：(x=0.40，y=0.59，z=0.0

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1)　C：(x=0.40, y=0.25, z=0.35) D：(x=0.06, y=0.59, z=0.35) を結ぶ線上およびこの線に囲まれる組成範囲にあり、かつwが、0.001≦w≦0.2の範囲にあり、MeがNi，Mg，Cu，Zn，Coのいずれか一種であり、かつMn，Cr，Feの少なくとも一種をそれぞれMnO_2，Cr_2O_3，Fe_2O_3に換算して、0．005～1．0重量％含有し、さらに主成分中のPbの一部が0．001～0．2のCa，Ba，Srの内少なくとも一種で置換するという技術的手段を採用した。

【0009】

【作用】主成分である$Pb(Ni_{1/3}Nb_{2/3})O_3-PbTiO_3-PbZrO_3$を上記範囲に限定した理由は、上記範囲以外の組成では電気機械結合係数Kpもしくは比誘電率εT_{33}著しく低下するからである。積層型圧電素子としたときに発生する歪量は圧電磁器組成物の材料特性のひとつである圧電歪定数に比例する。この圧電歪定数（d31）は数1により算出される。

【数1】

$$d31=\{(1-\sigma)S_{11}E\cdot\varepsilon T_{33}\cdot\varepsilon_0/2\}^{1/2}\cdot Kp$$

（σ：ポアソン比、$S_{11}E$：弾性コンプライアンス、ε_0：真空の誘電率）

数1の内σ，$S_{11}E$はPZT系の圧電材料では、たかだか$\sigma=0.25\sim0.35$、$S_{11}E=11\sim16\times10^{-12}m^2/N$の範囲にあるため、d31はKpと$\varepsilon T_{33}$の平方根の積にほぼ比例する。このため、上記限定範囲外では圧電歪定数（d定数）は著しく低下する。

【0010】$Pb(Me_{1/2}W_{1/2})O_3$（MeはNi，Mg，Cu，Zn，Coのいずれか一種）を0．001≦w≦0．2含有させると、KpとεT_{33}を低下させることなく、焼結温度を大幅に低下させることが可能となる。w＜0．001では焼結温度を1120℃以下とすることができない。w＞0．2ではKpの低下が著しい。Mn，Cr，Feの少なくとも一種をそれぞれMnO_2，Cr_2O_3，Fe_2O_3に換算して、0．005～1．0重量％添加するとKpとεT_{33}を低下させることなく、比抵抗を大幅に向上することができる。添加量が0．005重量％未満では比抵抗が大きくならず、添加量が1．0重量％を越えるとKpの低下が著しい。主成分中のPbをCa，Ba，Srの内少なくとも一種で置換するとεT_{33}が増加する。置換量が0．001未満では置換の効果が不十分で、0．2を越えるとKpの低下が著しく、かつ焼結温度が1120℃を越える。

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【0011】

【実施例】以下、実施例により、本発明の効果を具体的に説明する。酸化鉛（PbO）、酸化チタン（TiO_2）、酸化ジルコニウム（ZrO_2）、酸化ニッケル（NiO）、酸化ニオブ（Nb_2O_5）、酸化マンガン（MnO_2）、酸化鉄（Fe_2O_3）、酸化クロム（Cr_2O_3）、酸化タングステン（WO_3）、酸化マグネシウム（MgO）、酸化銅（CuO）、酸化亜鉛（ZnO）、酸化コバルト（CoO）、炭酸ストロンチウム（$SrCO_3$）の原料を表1および表2に示した組成となるように秤量し、これをボールミルで2時間混合した。得られた混合物を仮成形後、空気中において850℃で2時間仮焼し、更にボールミルで2時間粉砕した。これを造粒後プレス成形により直径20mm長さ15mmの成形体を作成した。この成形体をアルミナ若しくはマグネシアからなる容器内に密閉した状態で酸素中2時間の焼結を行った。得られた焼結体を切断、研磨加工により、直径16mm、厚さ0．8mmの素子にし、両端面にCr－Auからなる電極を形成し、シリコンオイル中において3kV／mmの直流電圧を15分間印加して分極処理を行った。

【0012】

【表1】

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No.	配合比 $Pb(Ni_{1/3}Nb_{2/3})O_3$ x	$PbTiO_3$ y	$PbZrO_3$ z	Sr置換量	Me	w	MnO_2添加量（重量%）
*1	0.74	0.25	0.01	−	−	−	−
*2	0.40	0.59	0.01	−	−	−	−
*3	0.40	0.25	0.35	−	−	−	−
*4	0.06	0.59	0.35	−	−	−	−
*5	0.739	0.25	0.01	−	Ni	0.001	−
6	0.739	0.25	0.01	−	Ni	0.001	0.005
7	0.495	0.3165	0.1485	−	Ni	0.01	0.01
8	0.495	0.3165	0.1485	−	Ni	0.01	0.05
9	0.495	0.3465	0.1485	−	Ni	0.01	0.1
10	0.495	0.3465	0.1485	−	Ni	0.01	1.0
*11	0.495	0.3465	0.1485	−	Ni	0.01	1.5
12	0.485	0.3395	0.1455	−	Ni	0.03	0.05
13	0.475	0.3325	0.1485	−	Ni	0.05	0.05
14	0.45	0.315	0.135	−	Ni	0.1	0.05
15	0.425	0.2975	0.1275	−	Ni	0.15	0.05
16	0.4	0.28	0.12	−	Ni	0.2	0.05
*17	0.375	0.2625	0.1125	−	Ni	0.25	0.05
18	0.4995	0.3497	0.1498	−	Mg	0.001	0.05
19	0.495	0.3465	0.1485	−	Mg	0.01	0.05
20	0.45	0.315	0.135	−	Mg	0.1	0.05

【0013】

20　【表2】

No.	配合比 $Pb(Ni_{1/3}Nb_{2/3})O_3$ x	$PbTiO_3$ y	$PbZrO_3$ z	Sr置換量	Me	w	MnO_2添加量（重量%）
21	0.4	0.28	0.12	−	Mg	0.2	0.05
22	0.4995	0.3497	0.1498	−	Cu	0.001	0.05
23	0.495	0.3465	0.1485	−	Cu	0.01	0.05
24	0.45	0.315	0.135	−	Cu	0.1	0.05
25	0.4	0.28	0.12	−	Cu	0.2	0.05
26	0.4995	0.3497	0.1498	−	Zn	0.001	0.05
27	0.495	0.3465	0.1485	−	Zn	0.01	0.05
28	0.45	0.315	0.135	−	Zn	0.1	0.05
29	0.4	0.28	0.12	−	Zn	0.2	0.05
30	0.4995	0.3497	0.1498	−	Co	0.001	0.05
31	0.495	0.3465	0.1485	−	Co	0.01	0.05
32	0.45	0.315	0.135	−	Co	0.1	0.05
33	0.4	0.28	0.12	−	Co	0.2	0.05
34	0.485	0.3395	0.1455	0.001	Ni	0.03	0.05
35	0.485	0.3395	0.1455	0.01	Ni	0.03	0.05
36	0.485	0.3395	0.1455	0.1	Ni	0.03	0.05
37	0.485	0.3395	0.1455	0.2	Ni	0.03	0.05
*38	0.485	0.3395	0.1455	0.25	Ni	0.03	0.05

【0014】表3および表4に各組成で得られた特性を示す。組成No.の1、2、3、4はそれぞれ図1のA、B、C、Dの組成でw＝0の時の組成に対応する。主成分である$Pb(Ni_{1/3}Nb_{2/3})O_3-PbTiO_3-PbZrO_3$がA、B、C、Dに囲まれた組成範囲内ではKp、$\varepsilon T_{33}$が大きく積層型圧電素子とした際に大きな変位量が得られる。組成No.5はNo.1の組成に$Pb(Ni_{1/2}W_{1/2})O_3$を添加した組成であるが、焼結温度が低下することが明らかである。組成No.6から11の結果よりMnO_2を添加することで比抵抗が大幅に向上することがわかる。No.11の結果よりMnO_2の添加量が1重量%を越えるとKpの低下が著しくアクチュエータ用の材料としては不適となることがわかる。No.12から17の結果から$Pb(Ni_{1/2}W_{1/2})O_3$の添加量が増えるにしたがって焼結温度は低下するが、wが0．2を越えるとKpが著しく低下することからwは0．2以下に限定した。組成No.18から33は$Pb(Me_{1/2}W_{1/2})O_3$のMeをそれぞれMg，Cu，Zn，Coとした時の特性を示す。いずれの場合もMeがNiの場合と同様の効果を示している。組成No.34から38の結果からPbの一部をSrに置換することによりεT_{33}がさらに大きくなるが，置換量が0．2を越えるとKpの低下が著しくアクチュエータ用材料として好ましくない。

【0015】表5および表6にはMnO_2の代わりにCr_2O_3を添加した場合、表7および表8にはMnO_2の代わりにFe_2O_3を添加した場合について、それぞれ組

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成および得られた特性を示す。いずれの場合もMnO₂を添加した場合と同様の効果が得られることがわかる。

【0016】

【表3】

No.	電気機械結合係数 (Kp)	誘電率 (εT_{33})	焼結温度 (℃)	比抵抗 ρ (Ω・cm)
*1	0.27	13500	1210	1.1×10^{10}
*2	0.39	1890	1220	1.2×10^{10}
*3	0.43	1750	1220	1.4×10^{10}
*4	0.55	1050	1280	1.3×10^{10}
*5	0.27	13200	1120	1.2×10^{10}
6	0.27	13210	1120	2.2×10^{13}
7	0.63	6130	1120	4.7×10^{13}
8	0.625	6090	1120	5.2×10^{13}
9	0.605	5890	1120	1.8×10^{14}
10	0.525	4860	1120	5.5×10^{13}
*11	0.30	3310	1120	6.4×10^{13}
12	0.61	5890	1090	5.6×10^{13}
13	0.60	5720	1070	3.5×10^{13}
14	0.555	5560	1050	5.9×10^{13}
15	0.52	5500	1040	4.6×10^{13}
16	0.40	5430	1030	3.3×10^{13}
*17	0.25	5280	1020	3.9×10^{13}
18	0.615	5790	1120	7.4×10^{13}
19	0.605	5650	1120	6.2×10^{13}
20	0.57	5330	1050	4.5×10^{13}

【0017】

【表4】

No.	電気機械結合係数 (Kp)	誘電率 (εT_{33})	焼結温度 (℃)	比抵抗 ρ (Ω・cm)
21	0.40	5020	1040	6.8×10^{13}
22	0.61	5920	1120	6.4×10^{13}
23	0.59	5800	1120	6.5×10^{13}
24	0.54	5460	1050	4.2×10^{13}
25	0.39	5310	1030	5.7×10^{13}
26	0.595	5560	1120	7.5×10^{13}
27	0.58	5360	1120	5.3×10^{13}
28	0.55	5210	1060	5.5×10^{13}
29	0.38	5110	1040	4.6×10^{13}
30	0.60	5890	1120	3.5×10^{13}
31	0.595	5830	1120	2.3×10^{13}
32	0.565	5450	1050	3.2×10^{13}
33	0.42	5220	1040	2.7×10^{13}
34	0.60	6150	1100	3.6×10^{13}
35	0.59	6290	1110	2.2×10^{13}
36	0.58	6460	1120	4.1×10^{13}
37	0.565	6520	1120	3.9×10^{13}
*38	0.42	6710	1150	2.3×10^{13}

【0018】

40　【表5】

No.	配合比 $Pb(Ni_{1/3}Nb_{2/3})O_3$ x	$PbTiO_3$ y	$PbZrO_3$ z	Me	w	Cr_2O_3添加量 (重量%)
39	0.495	0.3465	0.1485	Ni	0.01	0.01
40	0.495	0.3465	0.1485	Ni	0.01	0.05
41	0.495	0.3465	0.1485	Ni	0.01	0.1
42	0.495	0.3465	0.1485	Ni	0.01	1.0

【0019】

【表6】

9　　10

No.	電気機械結合係数 (Kp)	誘電率 (εT_{33})	焼結温度 (℃)	比抵抗 ρ ($\Omega \cdot cm$)
39	0.62	6070	1120	4.6×10^{13}
40	0.61	6010	1120	3.1×10^{13}
41	0.60	5830	1120	6.3×10^{13}
42	0.52	4740	1120	5.2×10^{13}

【0020】　　【表7】

No.	配合比 $Pb(Ni_{1/3}Nb_{2/3})O_3$ x	$PbTiO_3$ y	$PbZrO_3$ z	Me	w	Fe_2O_3添加量 (重量%)
43	0.495	0.3465	0.1485	Ni	0.01	0.01
44	0.495	0.3465	0.1485	Ni	0.01	0.05
45	0.495	0.3465	0.1485	Ni	0.01	0.1
46	0.495	0.3465	0.1485	Ni	0.01	1.0

【0021】　　【表8】

No.	電気機械結合係数 (Kp)	誘電率 (εT_{33})	焼結温度 (℃)	比抵抗 ρ ($\Omega \cdot cm$)
43	0.61	6050	1120	3.1×10^{13}
44	0.60	5920	1120	2.9×10^{13}
45	0.59	5740	1120	3.9×10^{13}
46	0.51	4680	1120	4.1×10^{13}

【0022】以上の結果から明らかなように、本発明の圧電磁器組成物は最適焼結温度が１１２０℃以下であり、比抵抗が大きく、かつKp、εT_{33}が大きい。なお、Srに代えてCa，Baを用いた場合も表1とほぼ同様の結果が得られた。

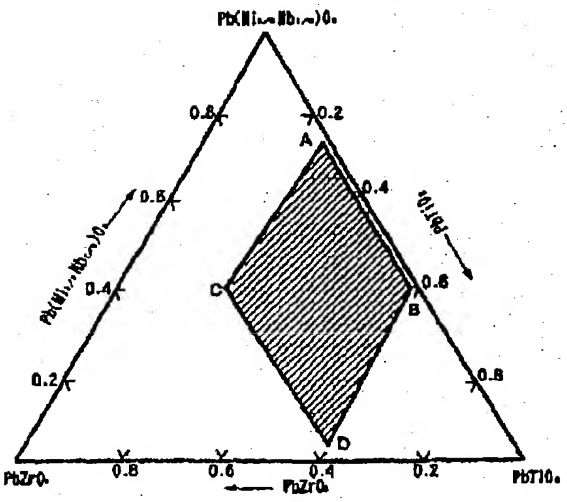
【0023】

【発明の効果】以上説明したように、本発明は、焼結温度が１１２０℃以下であることから、積層型圧電素子として利用する場合、安価な銀・パラジウム電極の使用が可能であり、しかも圧電歪定数が大きく、かつ、比抵抗も大きいことから、アクチュエータ、特に積層型圧電素子用材料として極めて有用である。

【図面の簡単な説明】

【図1】本発明における主成分（$Pb(Ni_{1/3}Nb_{2/3})O_3-PbTiO_3-PbZrO_3$）の組成範囲を示す。

【図１】



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(51) Int.Cl.⁵	識別記号	庁内整理番号	Ｆ Ｉ	技術表示箇所
Ｈ０１Ｌ　41/187				

PIEZOELECTRIC PORCELAIN COMPOSITION

Patent Number: JP5058645
Publication date: 1993-03-09
Inventor(s): WATANABE JUNICHI; others: 02
Applicant(s): HITACHI METALS LTD
Requested Patent: JP5058645
Application Number: JP19910222796 19910903
Priority Number(s):
IPC Classification: C01G53/00; C01G21/00; C04B35/00; C04B35/49; H01L41/187
EC Classification:
Equivalents:

Abstract

PURPOSE:To provide a material, sinterable at a low temperature, having a high resistivity and a large piezoelectric strain constant and useful as actuators, especially stacked type piezoelectric elements.
CONSTITUTION:The objective piezoelectric porcelain composition is expressed by the general formula (1-w)[xPb(Ni1/3Nb2/3)O3-yPbTiO3-zPbZrO3]-wPb(Me1/2 W1/2)O3 [(X+Y+Z) is 1] and the blending ratio (x), (y) and (z) are located on lines connecting the following composition points A; [(x) is 0.74; (y) is 0.25; (z) is 0.001] to B; [(x) is 0.40; (y) is 0.59; (z) is 0.01], C; [(x) is 0.40; (y) is 0.25; (z) is 0.35] and D; [(x) is 0.06; (y) is 0.59; (z) is 0.35] and within the range surrounded by the lines. Furthermore, (w) is within the range of 0.001<=(w)<=0.2 and Me is any one of Ni, Mg, Cu, Zn and Co. At least one of Mn, Cr and Fe is respectively contained in an amount of 0.005-1.0wt.% expressed in terms of MnO2, Cr2O3 and Fe2O3. Part of Pb which is the principal component is further replaced with 0.001-0.2 at least one of Ca, Ba and Sr.

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CLAIMS

[Claim(s)]
[Claim 1] It is shown by {xPb(nickel1/3Nb 2/3) O3-yPbTiO3-general formula (1-w) zPbZrO 3}-wPb (Me1/2W1/2) O3 (x+y+z=1), and a compounding ratio x, and y and z set to this 3 component composition diagram. Following forming point A:(X= 0.74, y= 0.25, z=.001) B: (x= 0.40, y= 0.59, z= 0.01) C: (x= 0.40, y= 0.25, z= 0.35) D: (x= 0.06, y= 0.59, z= 0.35) It is in the composition range surrounded by the line top to connect and this line, and w is in the range of 0.001<=w<=0.2. The piezoelectric-ceramics constituent which Me is any one sort of nickel, Mg, Cu, Zn, and the Co, and is characterized by the thing of Mn, Cr, and Fe for which a kind is converted into MnO2, Cr 2O3, and Fe2O3, respectively, and is contained 0.005 to 1.0% of the weight at least. [Claim 2] The piezoelectric-ceramics constituent according to claim 1 with which a part of Pb is characterized by the thing of calcium, Ba, and Sr of 0.001-0.2 replaced by kind at least.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] It is related with the piezoelectric-ceramics constituent which whose sintering temperature was as low as about 1100 degrees C, and was excellent in insulation performance about the piezoelectric-ceramics constituent with which this invention makes titanic-acid lead zirconate a principal component while especially the piezo-electric property was size.
[0002]
[Description of the Prior Art] Conventionally, as a piezoelectric-ceramics constituent, since a piezoelectric constant is size, it makes a piezoelectric transducer the start, and what makes titanic-acid lead zirconate a principal component is widely used as a material for actuators. However, the material of this system has the fault of being hard to guarantee the repeatability of a property, and homogeneity, in order that piezoelectric may be [that it originates in evaporation of the lead oxide at the time of baking, and is hard to obtain a precise sintered compact, and near the mol photograph pick phase boundary (MPB)] dependent on titanium and zirconium composition. In order to improve such a fault, there is a means to add oxides, such as a means to replace a part of Pb by calcium, Sr, Mg, Ba, etc. of optimum dose, or La, Nd, Nb, Ta, Sb, Bi, Th, W. According to the former, a dielectric constant can be made into size, without reducing a piezo-electric property, according to the latter, polarization becomes easy, a piezoelectric constant increases and there is an advantage that aging becomes small.
[0003] Many compound perovskite type compounds which, on the other hand, have two or more ion from which a valence differs in the position of A or B as an ABO3 type ferroelectric in parallel with improvement of the above-mentioned titanic-acid lead zirconate were discovered. Henceforth, the research and development to composition of three components with this compound perovskite type compound are furthered energetically. There is a thing of the composition which considers as the piezoelectric-ceramics constituent of the aforementioned three-component system, for example, becomes Pb(nickel1/3Nb 2/3) O3-PbTiO3-PbZrO3. It is that the material in which a mol photograph pick phase boundary (MPB) has the property which is expanded to a line from a point and suits a latus use more is obtained while the feature of such a piezoelectric-ceramics constituent of three-component system has little evaporation of a lead oxide and is easy to calcinate as compared with Pb(Zr, Ti) O3 of the aforementioned component system.
[0004] Since the piezo-electric distorted constant (d constant) is very large, the piezoelectric-ceramics constituent of the Pb(nickel1/3Nb 2/3) O3-PbTiO3-PbZrO3 aforementioned system fits the piezoelectric ceramics for actuator elements.
[0005]
[Problem(s) to be Solved by the Invention] However, the sintering temperature of the piezoelectric-ceramics constituent of the Pb(nickel1/3Nb 2/3) O3-PbTiO3-PbZrO3 aforementioned system is 1200-1300 degrees C and an elevated temperature. For this reason, when a laminating type piezoelectric device was created with this piezoelectric-ceramics constituent, platinum and palladium which can bear this sintering temperature as an internal electrode had to be used, and there was a problem that a

manufacturing cost was high. If sintering temperature can be made low, use of cheap silver, palladium alloy, etc. will be attained. Since an oxidation-reduction reaction is started and a crack and ablation are produced in a laminating type piezoelectric device while palladium sinters when there are many contents of that the cost of palladium is high when using silver and a palladium alloy as an internal electrode, and palladium, it is required that the rate of palladium should be 30% or less.
[0006] In order to make the ratio of palladium 30% or less, it is more nearly required than a Ag-Pd system phase diagram to make desirably 1150 degrees C or less of sintering temperature into 1120 degrees C or less. For this reason, complicated operation of having pulverized temporary-quenching powder creating the laminating type piezoelectric device which used silver and palladium for the internal electrode with the piezoelectric-ceramics constituent of Pb(nickel1/3Nb 2/3) O3-PbTiO3-PbZrO3 system, or carrying out HIP processing was needed. Furthermore, the piezoelectric-ceramics constituent of the Pb(nickel1/3Nb 2/3) O3-PbTiO3-PbZrO3 aforementioned system When specific resistance was comparatively small and the piezoelectric-ceramics constituent of the Pb(nickel1/3Nb 2/3) O3-PbTiO3-PbZrO3 aforementioned system is used for the element around 100 micrometers for much more thickness like a laminating type piezoelectric device for this reason, There was a problem of a low in reliability, such as pulling out or carrying out dielectric breakdown of performance in which the voltage which can be impressed is small and sufficient, during use.
[0007] this invention solves the trouble which exists in the above-mentioned conventional technology, and it aims at offering the piezoelectric-ceramics constituent with which sintering temperature is about 1100 degrees C and low temperature and with which specific resistance was suitable for the charge of actuator material, especially the charge of laminating type piezoelectric-device material in size while a piezo-electric property is size.
[0008]
[Means for Solving the Problem] In order to solve the above-mentioned problem, it sets to this invention. It is shown by {xPb(nickel1/3Nb 2/3) O3-yPbTiO3-general formula (1-w) zPbZrO 3}-wPb (Me1/2W1/2) O3 (x+y+z=1), and a compounding ratio x, and y and z set to this 3 component composition diagram. Following forming point A: (X= 0.74, y= 0.25, z=.001) B: (x= 0.40, y= 0.59, z= 0.01) C:(x= 0.40, y= 0.25, z= 0.35) D: (x= 0.06, y= 0.59, z= 0.35) It is in the composition range surrounded by the line top to connect and this line, and w is in the range of 0.001<=w<=0.2. Me is any one sort of nickel, Mg, Cu, Zn, and the Co, and even if there are little Mn, Cr, and Fe, a kind is converted into MnO2, Cr 2O3, and Fe2O3, respectively. It contained 0.005 to 1.0% of the weight, and the technical means that a part of Pb in a principal component replaced by kind at least among calcium, Ba(s), and Sr of 0.001-0.2 further were adopted.
[0009]
[Function] the reason which limited Pb(nickel1/3Nb 2/3) O3-PbTiO3-PbZrO3 which is a principal component to the above-mentioned range -- the composition of those other than the above-mentioned range -- an electromechanical coupling coefficient Kp or specific inductive capacity epsilonT33 -- it is because it falls remarkably It is ****** when it considers as a laminating type piezoelectric device. ****** is proportional to the piezo-electric distorted constant which is one of the material properties of a piezoelectric-ceramics constituent. This piezo-electric distorted constant (d31) is computed by several 1.
[Equation 1]
d31= [(1-sigma)S11 E-epsilon T33 and epsilon0 / 2] 1/2, Kp (sigma : a Poisson's ratio, S11E: an elastic compliance, epsilon0: dielectric constant of vacuum)
inner mho of several 1, and S11E -- the piezoelectric material of a PZT system -- at most -- sigma= -- since it is in the range of 0.25 to 0.35, and S11E=11-16x10-12m2/N, d31 is proportional to the product of Kp and the square root of epsilonT33 mostly for this reason, the above-mentioned limitation -- if out of range, a piezo-electric distorted constant (d constant) falls remarkably
[0010] It becomes possible to reduce sintering temperature sharply, without reducing Kp and epsilonT33, if Pb(Me1/2W1/2) O3 (Me is any one sort of nickel, Mg, Cu, Zn, and the Co) is made to contain 0.001<=w<=0.2 times. Sintering temperature cannot be made into 1120 degrees C or less in w<

0.001. The fall of Kp is remarkable at w> 0.2. Even if there are little Mn, Cr, and Fe, a kind is converted into MnO2, Cr 2O3, and Fe2O3, respectively, and specific resistance can be improved sharply, without reducing Kp and epsilonT33, if it adds 0.005 to 1.0% of the weight. The fall of Kp is remarkable, when specific resistance does not become [an addition] large at less than 0.005 % of the weight but an addition exceeds 1.0 % of the weight. If Pb in a principal component is replaced by kind at least among calcium, Ba, and Sr, epsilonT33 will increase. If the effect of substitution has the inadequate amount of substitution at less than 0.001 and it exceeds 0.2, the fall of Kp will be remarkable and sintering temperature will exceed 1120 degrees C.

[0011]

[Example] It is a book by the following and the example. A lead oxide (PbO), titanium oxide (TiO2), a zirconium oxide (ZrO2), Nickel oxide (NiO), a niobium oxide (Nb 2O5), manganese oxide (MnO2), An iron oxide (Fe 2O3), a chrome oxide (Cr 2O3), a tungstic oxide (WO3), Weighing capacity was carried out so that it might become the composition which showed the raw material of magnesium oxide (MgO), a copper oxide (CuO), a zinc oxide (ZnO), cobalt oxide (CoO), and a strontium carbonate (SrCO3) in Table 1 and 2, and this was mixed with the ball mill for 2 hours. Temporary quenching of the obtained mixture was carried out at 850 degrees C after temporary fabrication and into air for 2 hours, and the ball mill ground further for 2 hours. The with a diameter length [15mm length of 20mm] Plastic solid was created for this by after [a granulation] press forming. Where this Plastic solid is sealed in the container which consists of an alumina or a magnesia, sintering of 2 hours in oxygen was performed. The electrode which uses the obtained sintered compact as an element with a diameter [of 16mm] and a thickness of 0.8mm by cutting and polish processing, and becomes an ends side from Cr-Au about it was formed, 3kV [/mm] direct current voltage was impressed for 15 minutes into the silicone oil, and polarization processing was performed.

[0012]

[Table 1]

No.	配合比 $Pb(Ni_{1/3}Nb_{2/3})O_3$ x	$PbTiO_3$ y	$PbZrO_3$ z	Sr置換量	Me	w	MnO_2添加量 (重量%)
* 1	0.74	0.25	0.01	-	-	-	-
* 2	0.40	0.59	0.01	-	-	-	-
* 3	0.40	0.25	0.35	-	-	-	-
* 4	0.06	0.59	0.35	-	-	-	-
* 5	0.739	0.25	0.01	-	Ni	0.001	-
6	0.739	0.25	0.01	-	Ni	0.001	0.005
7	0.495	0.3465	0.1485	-	Ni	0.01	0.01
8	0.495	0.3465	0.1485	-	Ni	0.01	0.05
9	0.495	0.3465	0.1485	-	Ni	0.01	0.1
10	0.495	0.3465	0.1485	-	Ni	0.01	1.0
*11	0.495	0.3465	0.1485	-	Ni	0.01	1.5
12	0.485	0.3395	0.1455	-	Ni	0.03	0.05
13	0.475	0.3325	0.1485	-	Ni	0.05	0.05
14	0.45	0.315	0.135	-	Ni	0.1	0.05
15	0.425	0.2975	0.1275	-	Ni	0.15	0.05
16	0.4	0.28	0.12	-	Ni	0.2	0.05
*17	0.375	0.2625	0.1125	-	Ni	0.25	0.05
18	0.4995	0.3497	0.1498	-	Mg	0.001	0.05
19	0.495	0.3465	0.1485	-	Mg	0.01	0.05
20	0.45	0.315	0.135	-	Mg	0.1	0.05

[0013]

[Table 2]

No.	配合比 $Pb(Ni_{1/3}Nb_{2/3})O_3$ x	$PbTiO_3$ y	$PbZrO_3$ z	Sr置換量	Me	w	MnO_2添加量 (重量%)
21	0.4	0.28	0.12	-	Mg	0.2	0.05
22	0.4995	0.3497	0.1498	-	Cu	0.001	0.05
23	0.495	0.3465	0.1485	-	Cu	0.01	0.05
24	0.45	0.315	0.135	-	Cu	0.1	0.05
25	0.4	0.28	0.12	-	Cu	0.2	0.05
26	0.4995	0.3497	0.1498	-	Zn	0.001	0.05
27	0.495	0.3465	0.1485	-	Zn	0.01	0.05
28	0.45	0.315	0.135	-	Zn	0.1	0.05
29	0.4	0.28	0.12	-	Zn	0.2	0.05
30	0.4995	0.3497	0.1498	-	Co	0.001	0.05
31	0.495	0.3465	0.1485	-	Co	0.01	0.05
32	0.45	0.315	0.135	-	Co	0.1	0.05
33	0.4	0.28	0.12	-	Co	0.2	0.05
34	0.485	0.3395	0.1455	0.001	Ni	0.03	0.05
35	0.485	0.3395	0.1455	0.01	Ni	0.03	0.05
36	0.485	0.3395	0.1455	0.1	Ni	0.03	0.05
37	0.485	0.3395	0.1455	0.2	Ni	0.03	0.05
*38	0.485	0.3395	0.1455	0.25	Ni	0.03	0.05

[0014] The property acquired by each composition is shown in Table 3 and 4. 1, 2, 3, and 4 of composition No. correspond to the composition at the time of w= 0 by composition of drawing 1 of A, B, C, and D, respectively. In composition within the limits Pb(nickel1/3Nb 2/3) O3-PbTiO3-PbZrO3 which is a principal component was surrounded by whose A, B, C, and D, when Kp and epsilonT33 consider as a laminating type piezoelectric device greatly, the big amount of displacement is obtained. Although composition No.5 are the composition which added Pb(nickel1/2W1/2) O3 to composition of No.1, it is distinct that sintering temperature falls. It turns out that specific resistance improves sharply by adding MnO2 from the result of composition No.6 to 11. When the addition of MnO2 exceeds 1 % of the weight from the result of No.11, a bird clapper turns out to be unsuitable as a material for actuators with the remarkable fall of Kp. Although sintering temperature fell as the addition of Pb(nickel1/2W1/2) O3 increased from the result of No.12 to 17, since Kp fell remarkably when w exceeded 0.2, w was limited to 0.2 or less. Composition No.18 to 33 shows the property when setting Me of Pb(Me1/2W1/2) O3 to Mg, Cu, Zn, and Co, respectively. The effect same in any case as the case where Me is nickel is shown. Although epsilonT33 becomes still larger by replacing a part of Pb by Sr from the result of composition No.34 to 38, if the amount of substitution exceeds 0.2, the fall of Kp is not remarkably desirable as a charge of actuator material.

[0015] When Cr 2O3 is added instead of MnO2 in Table 5 and 6, composition and the acquired property are shown in Table 7 and 8, respectively about the case where Fe 2O3 is added instead of MnO2. It turns out that the same effect as the case where MnO2 is added in any case is acquired.

[0016]

[Table 3]

No.	電気機械結合係数 (Kp)	誘電率 (εT_{33})	焼結温度 (℃)	比抵抗 ρ (Ω・cm)
* 1	0.27	13500	1210	1.1×10^{10}
* 2	0.39	1890	1220	1.2×10^{10}
* 3	0.43	1750	1220	$1.4\times x10^{10}$
* 4	0.55	1050	1280	$1.3\times x10^{10}$
* 5	0.27	13200	1120	$1.2\times x10^{10}$
6	0.27	13210	1120	$2.2\times x10^{13}$
7	0.63	6130	1120	$4.7\times x10^{13}$
8	0.625	6090	1120	5.2×10^{13}
9	0.605	5890	1120	1.8×10^{14}
10	0.525	4860	1120	5.5×10^{13}
*11	0.30	3310	1120	6.4×10^{13}
12	0.61	5890	1090	5.6×10^{13}
13	0.60	5720	1070	3.5×10^{13}
14	0.555	5560	1050	5.9×10^{13}
15	0.52	5500	1040	4.6×10^{13}
16	0.40	5430	1030	3.3×10^{13}
*17	0.25	5280	1020	3.9×10^{13}
18	0.615	5790	1120	7.4×10^{13}
19	0.605	5650	1120	6.2×10^{13}
20	0.57	5330	1050	4.5×10^{13}

[0017]
[Table 4]

No.	電気機械結合係数 (Kp)	誘電率 (εT_{33})	焼結温度 (℃)	比抵抗 ρ (Ω・cm)
21	0.40	5020	1040	6.8×10^{13}
22	0.61	5920	1120	6.4×10^{13}
23	0.59	5800	1120	6.5×10^{13}
24	0.54	5460	1050	4.2×10^{13}
25	0.39	5310	1030	5.7×10^{13}
26	0.595	5560	1120	7.5×10^{13}
27	0.58	5360	1120	5.3×10^{13}
28	0.55	5210	1060	5.5×10^{13}
29	0.38	5110	1040	4.6×10^{13}
30	0.60	5890	1120	3.5×10^{13}
31	0.595	5830	1120	2.3×10^{13}
32	0.565	5450	1050	3.2×10^{13}
33	0.42	5220	1040	2.7×10^{13}
34	0.60	6150	1100	3.6×10^{13}
35	0.59	6290	1110	2.2×10^{13}
36	0.58	6460	1120	4.1×10^{13}
37	0.565	6520	1120	3.9×10^{13}
*38	0.42	6710	1150	2.3×10^{13}

[0018]
[Table 5]

No.	配合比 $Pb(Ni_{1/3}Nb_{2/3})O_3$ x	$PbTiO_3$ y	$PbZrO_3$ z	Me	w	Cr_2O_3添加量 (重量%)
39	0.495	0.3465	0.1485	Ni	0.01	0.01
40	0.495	0.3465	0.1485	Ni	0.01	0.05
41	0.495	0.3465	0.1485	Ni	0.01	0.1
42	0.495	0.3465	0.1485	Ni	0.01	1.0

[0019]
[Table 6]

No.	電気機械結合係数 (Kp)	誘電率 (εT_{33})	焼結温度 (℃)	比抵抗 ρ ($\Omega \cdot cm$)
39	0.62	6070	1120	4.6×10^{13}
40	0.61	6010	1120	3.1×10^{13}
41	0.60	5830	1120	6.3×10^{13}
42	0.52	4740	1120	5.2×10^{13}

[0020]
[Table 7]

No.	配合比 $Pb(Ni_{1/3}Nb_{2/3})O_3$ x	$PbTiO_3$ y	$PbZrO_3$ z	Me	w	Fe_2O_3添加量 (重量%)
43	0.495	0.3465	0.1485	Ni	0.01	0.01
44	0.495	0.3465	0.1485	Ni	0.01	0.05
45	0.495	0.3465	0.1485	Ni	0.01	0.1
46	0.495	0.3465	0.1485	Ni	0.01	1.0

[0021]
[Table 8]

No.	電気機械結合係数 (Kp)	誘電率 (εT_{33})	焼結温度 (℃)	比抵抗 ρ ($\Omega \cdot cm$)
43	0.61	6050	1120	3.1×10^{13}
44	0.60	5920	1120	2.9×10^{13}
45	0.59	5740	1120	3.9×10^{13}
46	0.51	4680	1120	4.1×10^{13}

[0022] The optimal sintering temperature is 1120 degrees C or less, the piezoelectric-ceramics constituent of this invention has large specific resistance, and Kp and epsilonT33 are large so that clearly from the above result. In addition, when it replaced with Sr and calcium and Ba were used, the almost same result as Table 1 was obtained.
[0023]
[Effect of the Invention] As explained above, since use of a cheap silver and palladium electrode is possible, and a piezo-electric distorted constant is moreover large and specific resistance is also large when using as a laminating type piezoelectric device, since sintering temperature is 1120 degrees C or less, this invention is very useful as an actuator, especially a charge of laminating type piezoelectric-device material.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] Conventionally, as a piezoelectric-ceramics constituent, since a piezoelectric constant is size, it makes a piezoelectric transducer the start, and what makes titanic-acid lead zirconate a principal component is widely used as a material for actuators. However, the material of this system has the fault of being hard to guarantee the repeatability of a property, and homogeneity, in order that piezoelectric may be [that it originates in evaporation of the lead oxide at the time of baking, and is hard to obtain a precise sintered compact, and near the mol photograph pick phase boundary (MPB)] dependent on titanium and zirconium composition. In order to improve such a fault, there is a means to add oxides, such as a means to replace a part of Pb by calcium, Sr, Mg, Ba, etc. of a proper quantity, or La, Nd, Nb, Ta, Sb, Bi, Th, W. According to the former, a dielectric constant can be made into size, without reducing a piezo-electric property, according to the latter, polarization becomes easy, a piezoelectric constant increases and there is an advantage that aging becomes small.
[0003] Many compound perovskite type compounds which, on the other hand, have two or more ion from which a valence differs in the position of A or B as an ABO3 type ferroelectric in parallel with improvement of the above-mentioned titanic-acid lead zirconate were discovered. Henceforth, the research and development to composition of three components with this compound perovskite type compound are furthered energetically. There is a thing of the composition which considers as the piezoelectric-ceramics constituent of the aforementioned three-component system, for example, becomes Pb(nickel1/3Nb 2/3) O3-PbTiO3-PbZrO3. It is that the material in which a mol photograph pick phase boundary (MPB) has the property which is expanded to a line from a point and suits a larger use is obtained while the feature of such a piezoelectric-ceramics constituent of three-component system has little evaporation of a lead oxide and is easy to calcinate as compared with Pb(Zr, Ti) O3 of the aforementioned component system.
[0004] Since the piezo-electric distorted constant (d constant) is very large, the piezoelectric-ceramics constituent of the Pb(nickel1/3Nb 2/3) O3-PbTiO3-PbZrO3 aforementioned system fits the piezoelectric ceramics for actuator elements.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The composition range of the principal component (Pb(nickel1/3Nb 2/3) O3-PbTiO3-PbZrO3) in this invention is shown.

[Translation done.]

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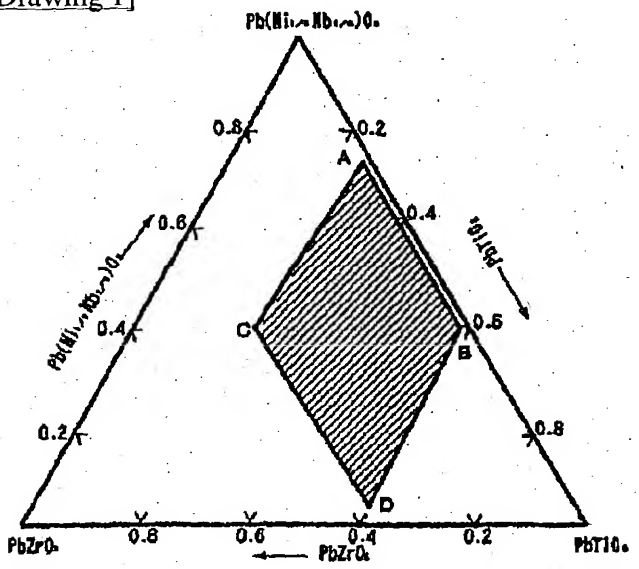
DRAWINGS

[Drawing 1]



[Translation done.]